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Protective layer and process and arrangement for producing protective layers

5 Description

The invention relates to a protective layer, in particular to a hard-material layer with a high scratch resistance and thermal stability, and to a process and apparatus for 10 producing protective layers.

The invention relates specifically to a protective layer for glass-ceramic plates, and to a process and arrangement for coating them, these glass-ceramic plates preferably being 15 used as cooking plates in cooking hobs and having a protective layer with a higher scratch resistance than the uncoated glass-ceramic on at least one side.

Modern cooking hobs have a glass-ceramic plate as the cooking 20 plate, the glass-ceramic plate typically being planar, although it may also be deformed in two or three dimensions. Glass-ceramic plates are both known from printed literature and commercially available, either in undecorated form or 25 decorated with thermally stable colors, e.g. ceramic colors. The cooking plate has individual cooking zones which are heated inductively, by electrically operated radiant heaters, by gas radiant heating elements or by alternative heating systems (for example DHS produced by SCHOTT).

30 Glass-ceramic plates typically have a Mohs hardness of from 5-6, which is comparable to that of steel, from which

cookware is typically produced. Everyday use, for example the cookware being put down and moved around, and the cooking plates being cleaned with abrasive cleaning agents and sponges or with a scraper, imposes a high mechanical loading 5 on the cooking hob, which can lead to traces of use being produced on the hob.

In addition, the cooking plate is often also used as an additional work surface in the cold state. In particular in 10 this state, there is a high risk of surface damage forming, for example through damage caused by rough bases of ceramic objects. All the surface damage incurred, over the course of time, leads to the formation of scratches on the surface, which is more or less noticeable to the user depending on the 15 selected illumination. An additional factor is that damage to the surface offers points of attack for soiling. The ease of cleaning of the surface becomes restricted, since it is much more difficult to clean dirt out of this damage. This effect is independent of whether the cooking hob is transparent, 20 colored or translucent.

The previous generation of glass-ceramic plates had a typical surface structure which was similar to orange peel. Although 25 these plates were also scratched as a result of the phenomena described above, they had a relatively low susceptibility to scratches on account of the additional surface structure. However, over the course of time, the surfaces of glass-ceramic plates have become smoother and shinier, which for the reasons mentioned above leads to an increased 30 susceptibility to scratching.

EP 0 716 270 B1 describes a cooking plate formed from glass-ceramic, on the top side of which a décor is provided, this cooking plate, in order to avoid scratches and traces of use, 35 having a protective layer in the form of enamel fluxes or a

silicate coating with a higher scratch resistance than glass-ceramic, with this protective layer covering the glass-ceramic cooking plate continuously or as continuously as possible, and a décor being printed onto this protective 5 layer or directly onto the glass-ceramic surface. It is preferable for the protective layer to be formed from a dark material. Although this protective layer in principle increases the mechanical load-bearing capacity of the glass-ceramic cooking plates, such that when the cooking plate is 10 in use the susceptibility to scratches can be reduced compared to an unprotected cooking plate, the enamel flux or silicate protective layers which are all that is disclosed by the EP document still do not offer optimum long-term 15 mechanical protection. Specifically, one drawback is that the protective layer itself represents a décor which is applied by means of screen printing. These décor colors are generally based on the same fluxes as the décor colors used for optical design purposes. Therefore, they are subject to the same restrictions in terms of abrasion. The minimum dimension of 20 décors of this type is of the order of magnitude of 0.5 mm, which is in any event visually perceptible and therefore interferes with the design, in particular if glasses or glass-ceramics with smooth surfaces are desired.

25 Furthermore, the explanations given do not allow any conclusions to be drawn as to the extent to which the proposed solution is compatible with the heater systems used. In particular the use of preferably dark materials as protective layer for glass-ceramics with a high IR 30 transparency and for radiant heaters will lead to restrictions in terms of the desired IR transparency and therefore to losses in terms of the initial cooking performance.

DE 100 00 663 A1 describes a process and the associated apparatus for providing an optically transparent body with a scratch-resistant layer of  $\text{Al}_2\text{O}_3$  over the entire surface by means of a modified PICVD process, in such a manner that a hard-material layer is formed, since it has been found that the known processes cannot be used to produce a sufficiently hard, dense, scratch-resistant and thermally stable layer, in particular from aluminum oxide. One drawback is the high cost of the process, in particular if large-area coatings have to be applied homogeneously. Hitherto, inhomogeneities have been inevitable, and this moreover has a long-term adverse effect on the visual appearance.

Furthermore, WO 96/31995 describes an inductively heated glass or glass-ceramic cooking plate with integrated coils, to which a hard-material layer of  $\text{Al}_2\text{O}_3$  is applied by means of the plasma spraying technique, in a layer thickness of between 50 and 200  $\mu\text{m}$ . One drawback in this context is that such thick layers are very rough, and therefore the use properties, such as the abrasion caused by pots and pans, manual abrasion and the cleaning properties are adversely affected. Furthermore, the appearance of the cooking plates having a layer of this type changes completely. The surface appears matt and gray.

Furthermore, it is known from DE 42 01 914 A1 (= US 5,594,231) to provide scanning windows made from glass or glass-ceramic for scanning systems, installed in tills in supermarkets and other retail markets, for detecting bar codes applied to the packaging of goods with a transparent hard-material layer on the top side, and then for a transparent coating with sliding properties to be provided on the hard-material layer, to make this scanning window more resistant to wear. Materials which are mentioned as being suitable for the hard-material layer include metal oxides,

such  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{SnO}_2$ ,  $\text{Y}_2\text{O}_3$ . Aluminum oxide which is deposited in amorphous form is referred to as being particularly suitable. In particular the amorphous deposition of the metal oxide in this context promotes the desired improved hardness and sliding properties of the protective layer. The hard-material layers described here are suitable for applications in the room temperature range, but their properties change at high temperatures, as are customary, for example, in the case of cooking plates, making them unsuitable for use at high temperatures. A protective layer for cooking plates requires materials which are able to withstand temperatures of up to  $800^\circ\text{C}$  and which are also able to tolerate the high thermomechanical stresses which occur between the glass-ceramic and the protective layer.

DE 201 06 167 U1 has disclosed a cooking hob with a glass-ceramic plate as cooking plate, this plate being provided with a transparent scratchproof layer which may be formed, *inter alia*, by a hard-material layer. Metal oxides, such as aluminum oxide, zirconium oxide, yttrium oxide, tin oxide, indium oxide and combinations thereof, are among the materials mentioned for this transparent layer. According to this document, the materials can be deposited, for example, using the sol gel technique, the CVD processes, in particular by means of the PICVD process, and by sputtering.

With the known processes for producing hard-material layers, such as for example those described in the abovementioned documents DE 42 01 914 A1 and DE 201 06 167 U1, the layers are typically deposited in an amorphous or partially crystalline structure. After prolonged use in the hot areas, or in the event of maximum thermal loading, layers of this type may undergo disadvantageous changes. For example, in these areas the layers may become discolored as a result of thermally induced compacting or may be opacified through

crystallization, with the result that the hot areas become optically perceptible. Furthermore, roughening in the range from 1 to 1000 nm may occur. The roughening alone may be optically perceptible, and the recesses which form 5 additionally make cleaning more difficult. The problem of crystallization in the hot areas is exacerbated by mechanical failure of the scratchproof layer. During crystallization, the structure of the layer changes, with the result that cracks are formed in the layer. The loss of lateral cohesion 10 means that the layer no longer offers any particular protection against scratching.

In order, for example, to impart a higher thermal stability to zirconium oxide, it is known (G. Wehl et al., Proc. CVD- 15 VII, 536 (1979)) to add what are known as stabilizers formed from yttrium oxide, magnesium oxide or calcium oxide to this component. However, a layer of this type, produced using the known processes, has a low density, which means that a layer of this type is porous.

20 The process described in US 4,920,014 for producing a layer of this type from stabilized zirconium oxide attempts to solve this problem by the layer being deposited in such a way, by means of the CVD process and accurately set process 25 parameters, such as temperature of the substrate, instant and duration of the supply of the reaction substances, etc., that it has only one or two crystal planes oriented parallel to the substrate surface. In addition to entailing very high process costs, crystalline layers of this type still have a 30 rough surface.

It is known from the field of turbine technology that layers 35 grown in column form have a particularly high resistance to rapid fluctuating thermal loads. For example, US 4,321,311 describes the use of a ceramic layer which is grown in

columnar form as thermal protection for metallic components used in turbine manufacture. However, on account of their coarse crystalline structures, the layers described in this document have a high roughness or porosity.

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Rough and porous surfaces quickly become dirty and are difficult to clean. Moreover, they are not visually clear and transparent, but rather are highly diffractive and are unsuitable for applications with visually attractive surfaces.

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The scratch resistance problems encountered with other optically transparent bodies formed from glass or glass-ceramic which are exposed to high use temperatures, for example chimney viewing windows, oven windows for pyrolysis ovens, etc., are similar to those encountered with cooking plates.

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The invention is based on the object of forming the protective layer for a body using economically advantageous coating processes which are in widespread use in industry, in such a manner that the layer is scratch- and wear-resistant, remains structurally stable and does not change visually in the event of thermal loading, and has a permanently smooth and visually attractive surface.

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This object is achieved by a protective layer as described in claims 1 to 24, a process as described in claims 25 to 41 and an arrangement as described in claims 42 to 49.

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The protective layer according to the invention for a body includes at least one hard-material layer comprising a metal oxide and/or metal nitride and/or metal carbide and/or metal oxynitride and/or metal carbonitride and/or metal oxycarbonitride, at least one of these hard-material layers

being interrupted by at least one interlayer that is different than the hard-material layer and is formed from metal oxide and/or metal nitride and/or metal carbide and/or metal oxynitride and/or metal carbonitride and/or metal oxycarbonitride. The hard-material layers form a basic building block for the function and properties of the protective layer and are also referred to below as functional layers.

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10 The interlayers which interrupt the functional layers are very thin layers compared to the functional layers. The interlayers interrupt the morphology of the functional layer. By suitable selection of the material and thickness of the interlayers and the spacing between them, it is possible to 15 influence the morphology of the functional layer in such a way that the functional layer grows in the form of very dense, narrow columns perpendicular to the substrate surface.

If the process parameters are selected in such a way that the 20 functional layers grow in a crystalline structure, it is possible to boost the positive properties of the layers, for example hardness, thermal stability and high resistance to scratching, still further.

25 The term crystalline is generally understood as meaning the state of solids with their particles arranged in a three-dimensional space lattice with a pronounced long-range order. The crystalline body, in this case the functional layer, may comprise a large number of small, irregularly supported 30 crystallites, or the lattice structure may continue through the entire layer. The crystalline columns which form in the functional layer with interrupting interlayers are column structures which are located closely next to one another and are formed predominantly perpendicular to the substrate. The 35 crystals predominantly have orientations which have little

tendency to widen out during columnar growth.

Typical layer thicknesses for scratchproof layers are in the range from 100 to 20 000 nm, and typical coatings for glass and glass-ceramic in the range up to 5000 nm. In this context, by way of example, interlayers with a thickness of less than 10 nm, preferably from 1 to 5 nm, which interrupt the functional layers at intervals of 30 to 500 nm, preferably from 50 to 250 nm, are particularly effective at achieving the desired properties, such as scratch and wear resistance, structural stability under thermal loads and permanently smooth, visually attractive surfaces which do not change visually.

Furthermore, to achieve the abovementioned properties, but mainly also under process engineering aspects, it is advantageous for the functional layers to be interrupted by interlayers at regular intervals.

To minimize the porosity of the protective layer and therefore also to minimize the roughness of its surface, in a manner which is cleaning-friendly, the functional layer and the interlayers which interrupt it are preferably formed in such a way that the lateral dimension of the columns is less than 1  $\mu\text{m}$ . In one particularly advantageous configuration, the lateral dimension of the columns is less than 200 nm. Moreover, the densely packed column structures allow substantially unimpeded optical transmission to be achieved and interfering effects caused by light scattering to be avoided.

In this context, functional layers made from silicon nitride or metal oxides in crystal phases have proven particularly suitable for transparent protective layers according to the invention.

It has been discovered that functional layers according to the invention formed from metal oxides, in particular from zirconium oxide with a stabilizing component comprising 0.5 to 50 mol% of  $\text{Y}_2\text{O}_3$ , preferably 1 to 10 mol% of  $\text{Y}_2\text{O}_3$  and particularly preferably 1.0 to 7.5 mol% of  $\text{Y}_2\text{O}_3$  with interlayers formed from silicon oxide, are particularly suitable for transparent, visually particularly attractive and highly temperature-stable (up to at most 800°C) protective layers.

In particular in order to avoid changes in the visual appearance of functional layers formed from stabilized zirconium oxide as a result of the use of interlayers, 15 interlayers formed from zirconium nitride are used. The zirconium nitride can be converted into zirconium oxide by means of a thermal aftertreatment step. Consequently, the interlayer has the same refractive index as the functional layer and is optically inactive irrespective of its 20 thickness. A further advantage is that only one reactive gas change is required during the reactive deposition of the layers.

Analogously to this procedure, zirconium can also be replaced 25 by other metals.

If interlayers formed from titanium-aluminum oxide are used, the refractive index  $n$  of these interlayers can be set in the range from  $1.55 \leq n \leq 2.50$  by setting the quantitative ratio 30 of titanium to aluminum, and can if appropriate be matched to that of a functional layer.

Interlayers of this type offer the possibility of varying the layer thickness of the interlayers, since they have no 35 influence, based on the functional layer, on the visual

appearance.

Moreover, within tight limits, the interlayers offer option of having a controlled influence on the visual appearance.

5 For this purpose, it is possible to select interlayers which have a refractive index that differs from that of the functional layer and the thickness of which is selected in such a way that they can become optically active. Further effects can be achieved by varying the distances between the  
10 interlayers.

Furthermore, it is possible for the protective layers also to include further hard-material layers, in particular transparent hard-material layers.

15 Hard-material layers formed from metal oxide and/or metal nitride and/or metal carbide and/or metal oxynitride and/or metal carbonitride and/or metal oxycarbonitride have a very wide range of layer morphologies and properties depending on  
20 the process conditions. To achieve good thermal stability, the aim is for the layer to be grown as far as possible in crystalline form. The interruption to the functional layer by very thin interlayers, preferably with a thickness of less than 10 nm, at intervals of from 30 to 500 nm, preferably from 50 to 250 nm, allows dense columnar, preferably dense  
25 columnar crystalline growth, of the functional layers in tight column structures, with the columns having only a low tendency to widen out, and on average preferably still only having a lateral dimension of less than 200 nm. As a result, these hard-material layers acquire a dense, smooth and visually attractive surface and are structurally stable under  
30 mechanical and thermal loads.

35 The protective layers according to the invention are suitable for coating a very wide range of bodies, which in particular

have to have a high resistance to scratching and a high thermal stability. Furthermore, they allow an attractive visual appearance and, depending on the layer material, also transparency. They are particularly suitable for use as 5 protective layers for glass, glass-ceramic or bodies formed from other nonmetallic, crystalline materials, without being restricted to these particular applications.

By way of example, it is possible to select interlayers to be 10 such that they are optically inactive in optical layer systems and improve the structural, mechanical and thermal properties of optical layer systems.

The protective layer is particularly advantageously suitable 15 for the coating of glass-ceramic cooking plates. The primary requirements in such applications are a high resistance to scratching, a high thermal stability and a visually attractive appearance, and these requirements can be satisfied by the coating according to the invention.

20 In the case of transparent protective layers, the glass-ceramic cooking plates or other bodies to be coated may additionally be decorated beneath or within the protective layer. The glass-ceramic cooking plates may additionally also 25 be decorated above the protective layer in the case of both nontransparent and transparent protective layers.

The process according to the invention for coating a body with a protective layer according to the invention 30 substantially comprises the steps of providing the body and the layer substances in a vacuum system and coating the body by means of a reactive physical vapor deposition process, with layer substances being produced in atomic dimensions and growing as a functional layer in columnar structures 35 substantially perpendicular to the body surface on the body.

The growth of a functional layer is interrupted at least once by the deposition of a very thin interlayer which, uninfluenced by the functional layer that has already grown, has a different morphology than the functional layer, so that 5 the tendency of columnar structures to widen out in the functional layer is interrupted.

A further process according to the invention for coating a body made from glass, glass-ceramic or another nonmetallic, 10 crystalline material, preferably for coating a cooking plate, with a protective layer according to the invention substantially comprises the steps of transferring the body into a vacuum system in order to be coated immediately after it has been produced and providing the layer substances and 15 coating the body by means of a reactive physical vapor deposition process, producing layer substances in atomic dimensions which grow as a functional layer in columnar structures substantially perpendicular to the body surface on the body. The growth of a functional layer is interrupted at 20 least once by the deposition of a very thin interlayer which, uninfluenced by the functional layer that has already grown, has a different morphology than this functional layer, so that the tendency of columnar structures to widen out in the functional layer is interrupted.

25 Physical vapor deposition processes with high levels of energy introduced and with high process temperatures, such as for example sputtering processes, are particularly suitable for the production of crystalline, column-like layer 30 morphologies.

However, not all sputtering processes are economically 35 suitable for industrial coating operations. In the context of this aspect, magnetron processes are particularly suitable for the coatings according to the invention.

Magnetron sputtering systems allow high coating rates in the low pressure range with relatively little heating of the substrate and their process parameters can be successfully controlled.

Vapor deposition processes with electron beam vaporizers are likewise suitable for the industrial production of layers, since in this case too it is possible to achieve good coating rates and to successfully control the process parameters. However, in this case additional bombardment with ions is required for coating processes according to the invention in order to obtain the high levels of energy introduction that are needed. The energy of the ions of the assisting ion beam is between 1 and 2500 eV, preferably between 1 and 800 eV, and particularly preferably between 20 and 450 eV.

A further advantage of this process is that the ion source can simultaneously be used to clean and activate the substrate.

Metal oxides are particularly suitable for coating a body with transparent protective layers. The layer starting materials are then in solid form as metallic components or as metal oxides.

In this context, it may be advantageous to feed into the vacuum system at least one additional gas, for example nitrogen, in order to optimize the material-removal rate during production of the layer substances and/or to optimize the degree of ionization of the reactive gas, and/or oxygen in order to optimize the oxidation of the layer.

In addition, oxidic layers which, for process technology reasons, have not been completely oxidized and therefore have

a disrupted crystal structure can be oxidized further, and thereby annealed by means of a subsequent heat treatment in an oxidizing atmosphere. The heat treatment can be carried out in a receptacle in which the coated body can be heated to 5 temperatures of up to 800°C, preferably to 400°C to 700°C. In addition, oxygen can be admitted to the receptacle. It is preferable for the oxygen partial pressures which are set to be between  $10^{-2}$  and 1000 mbar. The duration of the heat treatment should be between 1 minute and 10 hours, preferably 10 between 10 and 60 minutes.

Depending on the time within the overall production sequence, it may be necessary for the bodies which are to be coated to be subjected to a cleaning operation prior to the coating 15 operation. Cleaning will not necessarily take place if the coating operation immediately follows the final hot step in the production of a glass or glass-ceramic body, since this is when the surfaces are cleanest.

20 The cleaning of the objects to be coated can be carried out using at least one suitable cleaning bath with final drying in order to remove any soiling from the surface which is to be coated. Depending on the soiling which occurs, it may be necessary to use more than one cleaning bath and to apply 25 additional cleaning effects by heating and/or ultrasound excitation.

Furthermore, it is possible to carry out the cleaning in a 30 vacuum chamber by a plasma treatment with ions (examples of possible embodiments include bombardment of the substrate with ions from an ion source or "bathing" of the specimen in the plasma of a glow discharge), the energy of which is preferably in the range from 1 to 2500 eV, with preference from 50 to 1600 eV and particularly preferably from 100 to 35 500 eV. This results in particularly intensive cleaning of

foreign atoms and adsorbates of the surface. Suitable cleaning times are between a few seconds and a few minutes.

Moreover, it is advantageous to activate the surface of the body which is to be coated. The activation may likewise take place in a vacuum chamber, by means of a plasma treatment of the surface, as described above. The cleaning and activation may then if appropriate be carried out in a single process step.

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Before the coating operation starts and while the coating operation is being carried out, the body which is to be coated can be heated to the process temperature in the vacuum chamber. For this purpose, suitable heating elements are installed in the vacuum chambers. At the start of the process, the temperature of the body may be selected to be between room temperature and 800°C, preferably between 50°C and 550°C, particularly preferably between 100°C and 350°C.

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Furthermore, it may be desirable to achieve a particularly high surface quality for the body to be coated. For this purpose, the surface can be remachined once again in one or more polishing steps which are suitable for improving the slight surface roughness which remains down to an  $R_a$  value of 1 nm.

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According to the invention, a body made from glass, glass-ceramic or another nonmetallic, crystalline material, in particular a glass-ceramic hotplate, is coated with a protective layer, in particular with a protective layer according to the invention, using a coating installation and a production installation (1) which is directly connected to it via an entry lock (2.2) and substrate transfer station (2.1) and in which the substrate (8) to be coated has been produced immediately beforehand. The coating installation

comprises at least one coating chamber (4.n), which is a vacuum chamber, this chamber containing targets comprising the layer starting materials, excitation sources for generating layer starting materials in atomic dimensions, at 5 least one process gas inlet valve (15) for feeding process gases into the vacuum chamber, and shutters (7) as closable openings for supplying and discharging the substrate (8) which is to be coated.

10 The excitation source may be a magnetron sputtering source (13) or one or more electron beam vaporization source(s). These excitation sources can be used to achieve high coating rates for large-area coatings. In particular with double magnetrons (MF magnetron), the coating can be carried out 15 with a high degree of accuracy and stability.

In an advantageous embodiment, the coating installation has a cleaning/activation chamber (3), this chamber being a vacuum chamber and having at least one cleaning/activation ion beam source (11) for cleaning and/or activating the substrate (8) arranged between the input lock (2.2) and the coating chamber 20 (4.1) and connected to the latter via shutters (7).

To produce protective layers having a plurality of functional 25 layers made from different layer starting materials, it is possible either to arrange a plurality of targets A (14) in just one coating chamber (4.1) or to provide a corresponding number of further coating chambers (4.n).

30 To produce the interlayers, it is possible either to arrange a further target B (12) comprising the layer starting material for the interlayer in the coating chamber (4.1) or to provide a further coating chamber (4.2) containing the target B (12).

Further arrangements and combinations of coating chambers (4.n) and targets are also conceivable and possible, depending on the layer structure and process sequence.

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To further optimize metal oxide layers, it is advantageous for these layers to be aftertreated in an oxygen atmosphere. For this purpose, the coating installation includes an aftertreatment chamber (5), which is likewise a vacuum chamber and includes at least one oxygen feed valve (16) and heating elements (9) and is connected via shutters (7) to the coating chamber (4.1) or a further coating chamber (4.n).

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It is preferable for the coating chambers (4.1, 4.n) and the cleaning/activation chamber (3) to include heating elements (9) for heating the substrate (8) and realizing an optimum heating concept during the coating of the substrate (8).

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After coating of the substrate (8) and if appropriate aftertreatment of the layer, the substrate is passed out of the coating installation via an exit lock (6.1) and substrate discharge unit (6.2). The exit lock (6.1) is connected to the final vacuum chamber in the processing sequence via a shutter (7).

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The invention is to be explained in more detail below on the basis of an exemplary embodiment. In the drawing:

Figure 1: shows a magnetron sputtering installation

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Protective layers, in particular transparent, visually attractive, structurally and thermally stable scratchproof layers, for example of zirconium oxide in a stabilized crystal phase, in particular yttrium-zirconium oxide, can be applied to a glass-ceramic hotplate over a large area and

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using a process which is eminently suitable for use on an industrial scale by means of a magnetron sputtering installation as shown in figure 1.

5 Substrate transfer:

The substrate (8), for example a CERAN plate for cooking hobs, with dimensions of 60 cm x 60 cm, immediately after it has been produced, following the final hot step of ceramicization, is transferred from the production 10 installation (1) into the coating installation. The coating installation is a vertical installation which allows the substrates (8) to be coated without edges being formed. The substrates (8) are transferred individually into the coating installation.

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After a substrate (8) has been transferred into the substrate transfer station (2.1), the latter is closed and a pressure of < 1 mbar is set. Then, the substrate (8) is transferred via a shutter (7) into the entry lock (2.2). The entry lock 20 (2.2) is evacuated, so that a pressure of <  $10^{-2}$  mbar is established therein.

In general, the further transfer of the substrate (8) from one process unit to the next within the sputtering 25 installation takes place via the shutters (7).

The substrate is then transferred into the cleaning/activation chamber (3).

30 Substrate cleaning and activation:

The cleaning and activation chamber (3) is likewise a vacuum chamber in which there are heating elements (9) for heating the substrate (8) and cleaning/activation ion beam sources (11).

Cleaning does not necessarily have to be carried out, since the coating immediately follows the final hot step in production. If appropriate, the cleaning of the substrate (8) 5 may be carried out in a single step together with the activation of the surface of the substrate (8).

The cleaning/activation chamber (3) is initially evacuated to a process pressure of  $< 5 \cdot 10^{-5}$  mbar, and the substrate (8) is 10 heated to a temperature of up to approx. 700°C. Since the substrate (8) has been transferred to the coating operation immediately after the final hot step of ceramicization, heating to these high temperatures involves much lower costs than is the case in known processes.

15 Then, for cleaning and activation purposes argon ions with an energy of approx. 400 eV are fired onto the surface of the substrate (8) in the cleaning/activation chamber (3). The substrate (8) moves continuously forward at a rate of approx. 20 3 cm/min. Then, the substrate (8) is transferred into the coating chamber (4.1).

#### Coating:

25 The first coating chamber (4.1) is likewise a vacuum chamber and is used for coating with a first starting material for a functional layer. This is followed by a further coating chamber (4.2), which is used to interrupt the coating with the functional layer; the coating with the interlayer takes 30 place in this further coating chamber. If the coating is to comprise still further layers formed from different starting materials or if the coating of a plurality of substrates (8) is to be carried out in parallel, it is also possible to add further coating chambers (4.n).

In the first coating chamber (4.1) there is a target A (14) comprising the layer starting material for the functional layer, and in the second coating chamber (4.2) there is a target B (12) comprising the layer starting material for the interlayer. Heating elements (9), diaphragms (10) and magnetron sputtering sources (13) are arranged in each of these and any other required coating chambers (4.n), with the targets A and B (12, 14) being located directly on the magnetron sputtering sources (13).

The substrate (8) is held at the desired process temperature by means of the heating element (9). The layer starting material for target A (14) for the functional layer is metallic zirconium-yttrium. This material is atomized with the aid of the magnetron sputtering sources (13). The magnetron sputtering sources (13) are MF magnetrons (length 1 m, 40 kHz, 20 kW) which are operated in transition mode. The process gas inlet valve (15) is integrated in the magnetron sputtering source (13) and comprises a plurality of valves distributed over the length of the MF magnetron. The supply of oxygen, by means of a specific control arrangement known to the person skilled in the art, causes the magnetron sputtering source (13) to operate in what is known as the transition mode. In this mode, oxygen is supplied via the process gas inlet valve (15), so that an yttrium-zirconium oxide film is formed on the substrate (8). The diaphragms (10) define a coating window over the entire length of the substrate (8) with a width of 40 cm.

Then, by suitable movements, the substrate (8) is homogeneously coated with a layer thickness of 150 nm over the coating window. It is then transferred to the second coating chamber (4.2), in which an interlayer of silicon oxide with a layer thickness of 5 nm is applied in order to

interrupt the functional layer which was previously grown. The magnetron sputtering source (13) used to apply this layer is a pulsed DC magnetron (pulse frequency 100 kHz, power 10 kW) with a silicon target B (12). Suitable addition of 5 oxygen via a process gas inlet valve (15) causes the silicon oxide film to form. The process gas inlet valve (15) is likewise coupled to the magnetron sputtering source (13).

10 The substrate (8) is transferred back into the first coating chamber (4.1) and the coating operation with yttrium-zirconium oxide is continued. These operations are repeated until the protective layer has reached a thickness of 2.01 µm (13 sublayers of yttrium-zirconium oxide of 150 nm each and 12 silicon oxide interlayers of 5 nm each = 2010 nm). After 15 the coating operation, the substrate (8) is transferred into the aftertreatment chamber (5).

#### Aftertreatment:

20 The aftertreatment chamber (5) is a vacuum chamber with heating elements (9) and an oxygen feed valve (16).

The substrate (8) is heated to temperatures of > 400°C and an elevated oxygen partial pressure of > 10<sup>-2</sup> mbar is set in the chamber in order to ensure complete oxidation of the layer.

25 In principle, it is also possible for this aftertreatment to be carried out outside the coating installation. Following the aftertreatment, the substrate (8) is transferred into the exit lock (6.1), which is then vented to atmospheric pressure. The fully coated substrate (8) leaves the coating 30 installation via the substrate discharge station (6.2).

35 The coated CERAN cooking plate obtained in this way has a greatly increased resistance to scratching compared to an uncoated cooking plate. The coating is able to withstand

mechanical loads, is structurally stable under thermal loads of up to 800°C and has an attractive optical design.